RUBY

An Electically Controlled,

Adiabatic Calorimeter

Chemical Engineering

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AN ELECTICALLY CONTROLLED,
ADIABATIC CALORIMETER

BY

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THESIS

FOR THE

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THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

Irving Randolph Ruby

ENTITLED   An Electrically Controlled Adiabatic Calorimeter

IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

DEGREE OF   Bachelor of Science in,

                    Chemical Engineering.

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HEAD OF DEPARTMENT OF *Chemistry*

OUTLINE FOR THESIS

        Subdivisions of the

Description of the Calorimeter Proper.

I.   Vessels for holding liquids, baths, etc.

II.   Stirrers for the baths.

III. Measurement of the temperature.

IV. Measurement of the temperature difference.

V.   Heaters for the inner and outer liquids.

VI. Measurement of the energy of dilution.

Introduction.

The purpose of this thesis is to develope a calorimeter in which it shall be possible to measure such small quantities of heat as are evolved, for example, in the dilution of alcohol solutions. The calorimeter which has been developed for such work embodies in combination several ideas which have been used singly by other investigators.

Since the temperature change which is involved is a small one, several fundamental parts of the process of heat measurement have been carefully considered and the apparatus and the method employed which would give the most accurate results. Several conditions have made it practicable to use a thermometer which would give more accurate temperature readings than those obtainable from the mercury thermometer . To measure temperature to 1/10,000 of a degree the most practicable is a delicate platinum resistance thermometer. This method is not an uncommon one and will be described in more detail later.

Another important consideration is the transfer of heat between the calorimeter vessel and its surroundings. T. W. Richards and his associates in their work on the "Determination of the Heat of Solution of Metals in Acids"* described an adiabatic apparatus- one which kept the solution at the same temperature as the surrounding bath to insure no exchange of heat. We have embodied this idea to some extent but have varied from the strict adiabatic idea somewhat in that we have balanced the heat of stirring the inner solution, the evaporation effects etc., by a constant difference of temperature between bath and solution and this
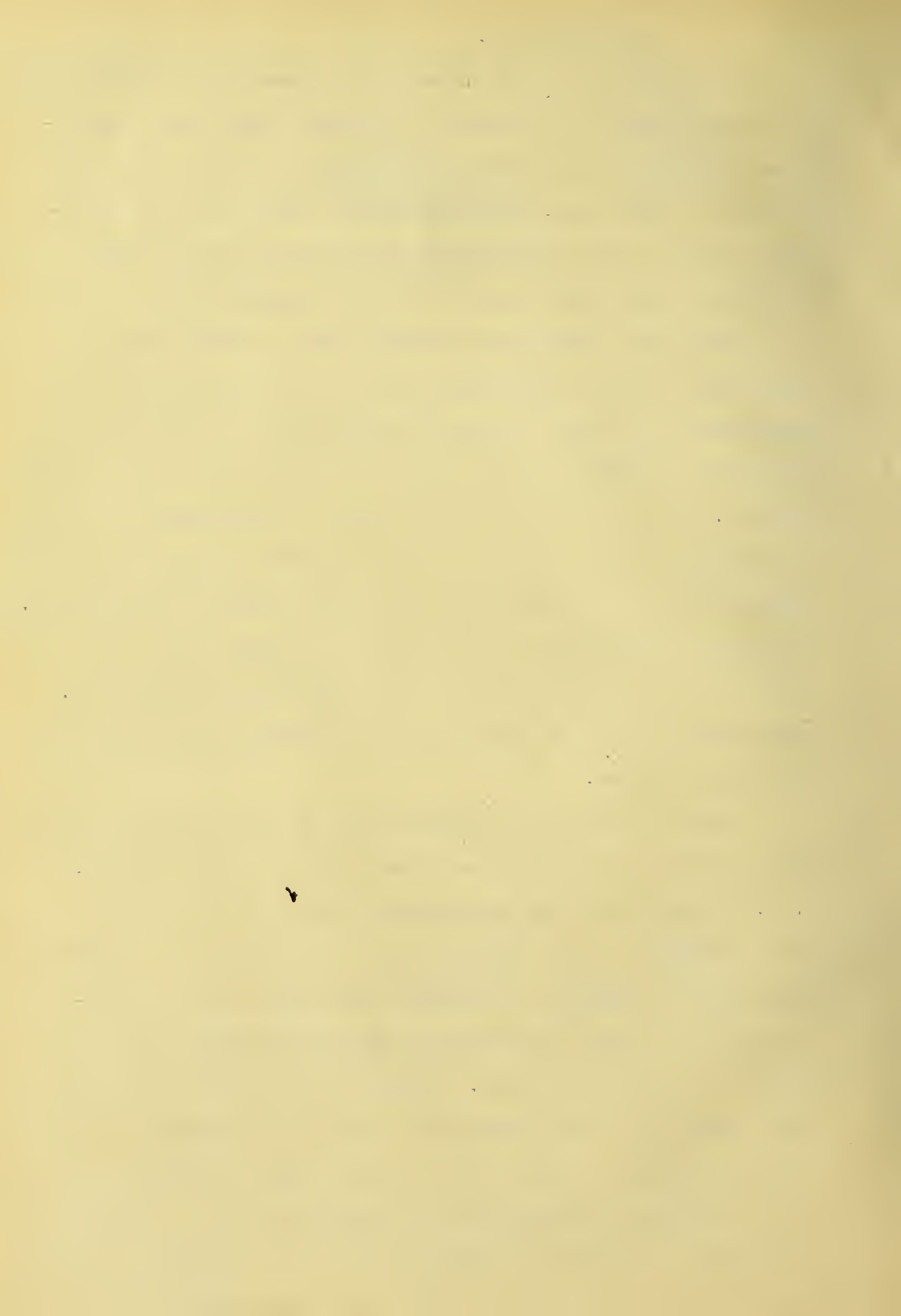
difference, when maintained, has enabled us to avoid the
usual corrections in calculating the results. The Broca
galvanometer which we used to get accurate readings with
the platinum resistance thermometer, has a slow period and
hence it was essential that the temperature should remain
constant over long periods- at least for several minutes.
Reference to the trial run will show that this was accom-
plished.

For the purpose of accurate work in calculating our
heat data for a given solution we need accurate data as to
the heat capacity of the calorimeter. This is obtained by
our method of passing in an accurately measured amount of
electrical energy (after the temperature rise due to the
dilution) and noting the resulting change of temperature.
The electrical measurement of a heat rise has been used
with success by Jaegar and Steinwehr (Ann der Physik, 326-
23) in their work on the calibration of a bomb calorimeter.

The size of the *calorimeter* ~~solution which~~ we used has many advan-
tages as for example the low tendency for evaporation effects
due to the small surface exposed for a given volume. The
size as used does not seem absolutely essential and a smaller
size may be planned in the future.
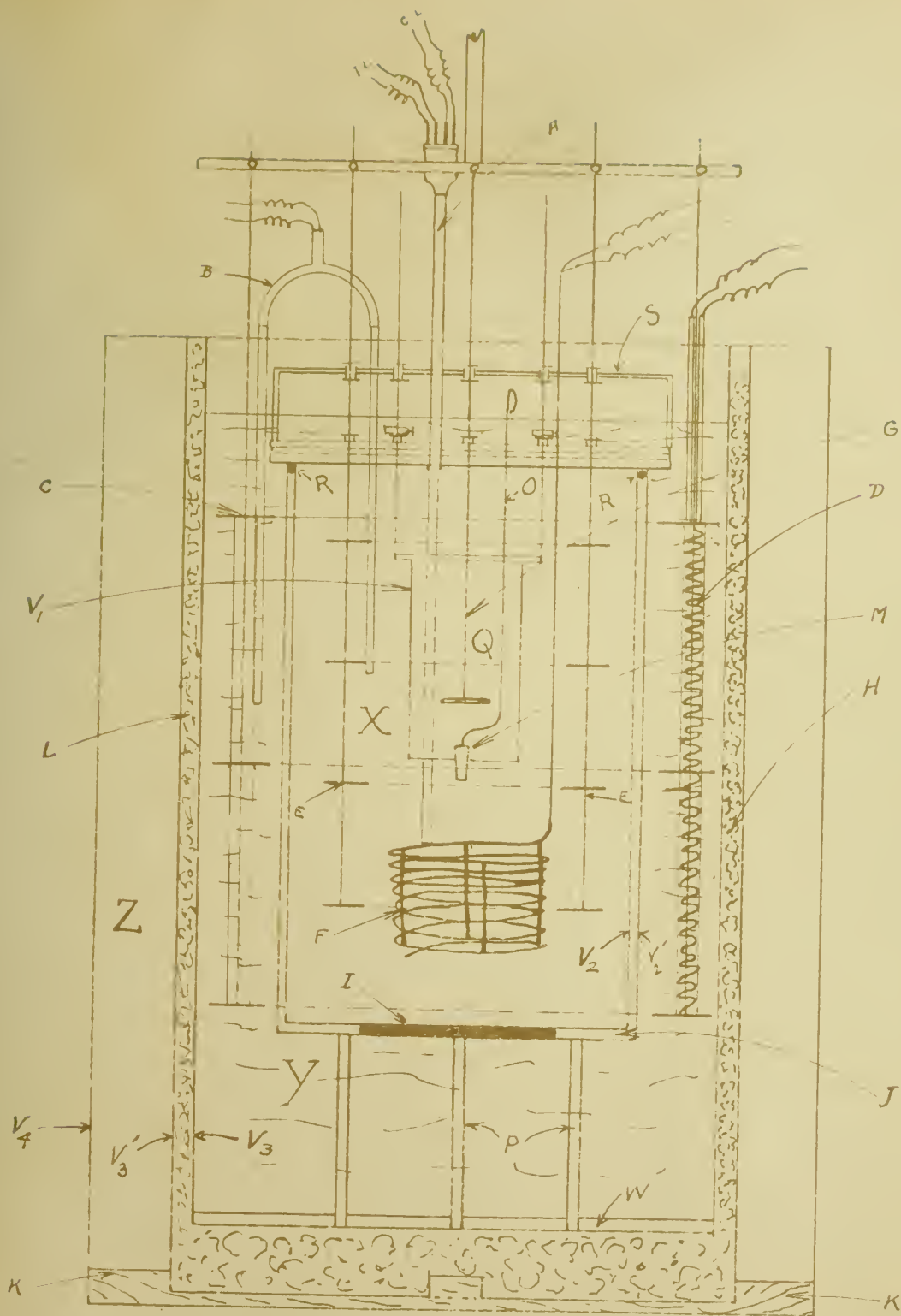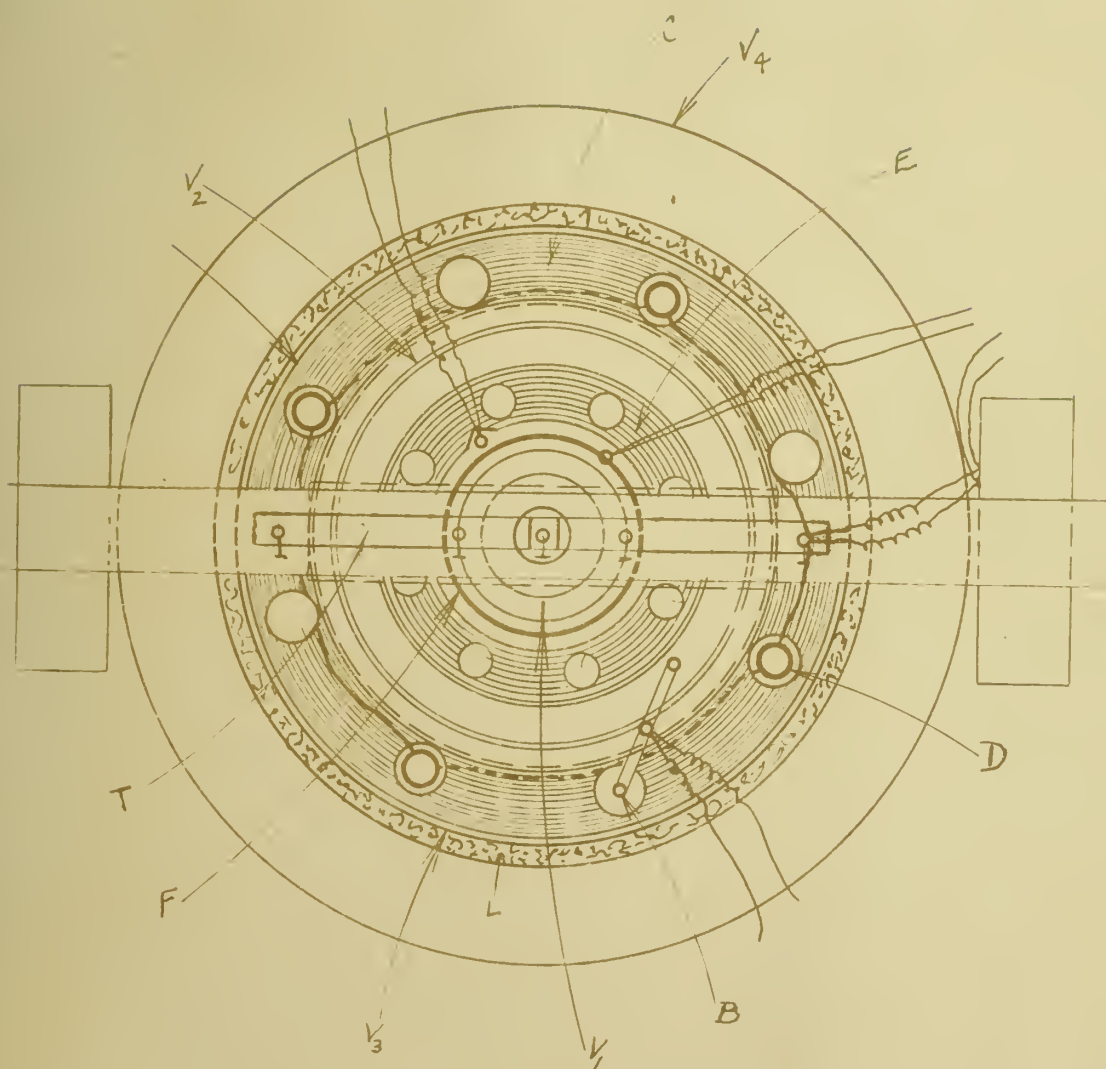
SECTION OF CALORIMETER.
FIG I.
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Description of the Calorimeter Proper.

I. Vessels for holding the liquids, baths, etc.

The calorimeter, as finally worked out, may be des-
cribed as follows: The vessel (V_2 Fig. I) for holding the
liquid in which the dilution is to be made is a brass can
heavily nickel-plated and capable of holding a little over
ten liters. It is $13\frac{1}{4}$ inches high and has a diameter of $8\frac{1}{2}$
inches with walls 1/16 of an inch thick. This vessel rests
inside another vessel of similar construction but provided
with a 3/4 inch flange at the top and with a diameter of 9
inches so that there is a $\frac{1}{4}$ inch air space surrounding the
vessel V_2 to act as an insulator. A hard rubber disc (D)
supports V_2 at the bottom and a ring of rubber tubing (R)
fits tightly between the two vessels, V_2 and V_2', as shown
and provides equal spacing of the air gap. This ring also
prevents the passage of any water into the air space (J)
where its peesence might cause large errors in the temper-
ature measurement due to the results of evaporation. The
vessel V_2'' is supported upon three hollow brass pipes (P)
which are securely brazed to it. These fit into holes in
the wooden plate (W) and any movement of the vessels during
a run is prohibited. The next outer vessel (V_3) is a large
galvanized iron can about 22 inches deep by 13 inches across
so that there is a 2 inch space between V_2 and V_3 for the
constant difference bath. A second outer can (V_3') is separ-
ated from V_3 by a $\frac{1}{2}$ inch space which is filled with woolen
felt. The outermost can (V_4) is 18 inches across by 24
inches deep and the space (Z) between it and the last men-

· TOP VIEW OF CALORIMETER ·

FIG ·II·

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tioned vessel can be filled with water or ice as the occa-
sion may demand. The purpose of the outermost bath is to
maintain the water (Y) at a certain temperature as near as
possible to a constant value or at least within such a
range as to be readily controlled by means of the heater (D).
Returning to the interior of the apparatus- the small can
(V_1) holds the liquid (Q) which is to dilute the liquid (X),
in vessel V_2. Its dimensions are 5 inches high by 2 3/4
inches across and its capacity is about 485 cubic centimeters.
A hole 3/4 inches across is provided in the bottom into
which a rubber stopper (M) is so arranged that it can be
readily pushed out by means of the brass rod (O) thereby
allowing the liquids to mix. The vessel (V1) is supported
by brass rods running out through the cover. These may be
clamped so that the can is at any desired height in the li-
quid X, or so that it can be lowered to allow a complete
mixing. The vessel V_2' is fitted with a stout brass cover
to which the guide plate (S) is fastened. This plate acts
as a brace and a guide for the various stirring rods etc.
Two pure rubber gaskets fit between the flange on vessel
(V_2') and the cover, as shown, and these provide a tight
seal when clamped together by the eight equally spaced
clamps. The cover to the can is provided with holes for
all the necessary thermometers, stirrers, etc. as shall
be described.

II. Stirrers for the baths.

One of the most important considerations in an exper-
iment where so large a quantity of liquid is to be maintain-
ed within such small limits of temperature, is that of per-

fect stirring. After trying out several systems such as propellor blades on a vertical shaft, etc., the type of stirrer shown was finally adopted. The stirrer used for the liquid Y consists of three discs of heavy galvanized sheet iron, spaced 5 inches apart and braced by vertical rods. These discs have an outside diameter of $12\frac{1}{2}$ inches and are 15/8 inches across giving an area of 66.1 square inches per disc, allowing for the holes. Eight holes 3/4 inches across are spaced evenly around the disc and of these four are open so as to allow a free passage of the liquid on stirring. The other four holes alternating with these are traversed by vertical hard glass tubes 3/4 inches in diameter in which the heater coils of nichrome wire for this bath are placed. The liquid X is stirred by a stirrer like the one just described except for the size and the absence of heating coils. Its discs of which there are four, are 3 inches apart, measure 1 inch wide, and are 7 inches in diameter. Allowing for the eight 5/8 inch holes for the passage of the liquid, each disc presents a surface of 10 square inches of stirring area. The innermost liquid Q is stirred by a simple disc $1\frac{1}{2}$ inches in diameter and fastened to the end of a brass rod.

All of these stirrers connect to a cross arm (T) above the apparatus, and this connects in turn to an eccentric which gives the arm an up and down motion of about 2 inches at the rate of one complete motion per second. The power used to drive the mechanism is a 1/6 horse-power A.C. motor, but a larger source of power is to be recommended for the

work as the motor showed signs of overload very often.
The power was transmitted by means of leather belting, and
this too should be supplimented by a more positive means
of power transmission, such as worm gearing would provide,
for as will be seen the rate of stirring should be kept
constant in order that certain corrections may be omitted.
The agitation provided by this system of stirring proved
most satisfactory and temperature differences were found
to equalize in a remarkably short time considering the
degree to which any temperature differences could be detect-
ed by the devices used.

III.- Measurement of the temperature.

The temperature of the liquid X is measured to an
accuracy of 1/10,000 of a degree C. by a delicate platinum
resistance thermometer whose internal resistance is about
25 ohms. The current is supplied to it by a new dry cell
and the changes in resistance and therefore current are re-
corded by the use of a Leeds and Northrup Wheatstone bridge.
This bridge is shown in Fig. No. III. It is provided with
two arms of 100 ohms each(this can be made 1000 ohms if
desired). Into one of the other two arms is connected the
platinum resistance thermometer while the remaining arm
contains, in series, the compensating leads and four decade
series of 10, 1, .1, and .01 ohms each, together with a
manganin bridge wire of large diameter and variable length
and consisting of eleven turns. These turns can be made
equal to 1, .1, or .5 ohms by connecting shunt coils in
parallel. In all the work done the turns were kept constant-
ly equal to .1 ohm each. Each turn of the bridge wire is

divided into 200 parts on the scale and as each part is about

3 mm. long the readings may be easily made to 1/5 of a $\overset{\text{vis}}{\wedge}$sion.

This 1/5 of a division corressponds to 1/100,000 of an ohm

or in the 25 ohm resistance to 1/10,000 of one degree C. This

was checked out by experiemnt.

The thermometer itself is similar to that used by Dick-

enson and Mueller (Bulletin Bureau Standards Vol. III, No.4)

in many respects. A platinum wire wound on a mica strip is

sheathed in a platinum tip about 8 inches long. This tip is

joined carefully to a glass tube and the leads, two resistance

and two compensating, are carried out through an air tight

and moisture tight joint which is carefully packed with P_2O_5.

In this apparatus a brass tube was so arranged on the cover

of the calorimeter as to allow the thermometer to extend about

half way down into the liquid X, and so as to protect the

delicate instrument from injury.

The calibration of the resistance thermometer in order

to get exact temperature readings in terms of the usual units

was not necessary, as the thermometer is used merely as a

very sensitive thermoscope, i.e. to measure the ratio of the

heat of any given rise and the heat passed into the solution

by a known current. Our determinations of heat effects are$\overset{\text{therefore}}{\wedge}$

independent of any specific heat data.

IV.- Measurement of the temperature difference.

As has been mentioned, the liquid Y must be kept enough

colder than X so that the heat exchange from X to Y is just

equal to the heat developed in X by the stirring. This diff-

erence is determined for each particular set of conditions

at the beginning of a run, and is indicated by a manganin-
copper thermo- couple. This consists of 14 junctions in each
of two brass tubes. One tube dips into X and one into Y (See
B, Figs. I and II) so that any difference of temperature
between these two sets up a current which, by suitable conn-
ections through a galvanometer, can be easily read to .01 of
a degree C. The height of the liquid on the sides of the tubes,
or in other words
the amount of each
couple which is ex-
posed to the diff-
erence in tempera-
ture, affects the
reading as is to
be expected. As we
care here for rel-
ative values only,
and since the value
of this difference
differs for each run,
the only essential
point to watch is

General view of apparatus.

L. & N. Potentiometer at left;
Wheatstone bridge at center;
Galvanometers are to the left rear;
Calorimeter can visible just
beyond the table.

that the height of the liquid on the couple shall remain con-
stant throughout any one run. This is accomplished by fasten-
ing the outer tube in place and by means of a rubber sleeve
on the inner tube which allows it to enter the hole provided
to a certain distance only. The variation of the height of the
liquid in the process of stirring is not sufficient to cause

any fluctuations.

VI.- Heaters for the liquids X and Y.

The heating of the bath Y is accomplished by passing
a 110-volt A.C. current through the coils of a nichrome wire
in the glass tubes of the stirrer C. As shown in Fig..II

the current goes down
in one coil and across
the bottom of the stir-
rer to the next glass
tube, then up this
and over to tube num-
ber three, etc. The
total resistance of
the coil is about 80
ohms . The spring
switch placed at the
hands of the operator
throws the current
on. The inner heater

View of the apparatus with
calorimeter in foreground.
Wheatstone bridge at center.

is a coil of copper tubing through which an insulated man-
ganin wire passes. The current, passing down the tube to the
end is transmitted to the wire by a soldered joint and the
circuit is complete. The connections for this heater are made
by a switch connecting with storage cells. The switch, by re-
versing it, can be made to connect with a depolarizing resist-
ance which is as near equal to the resistance of the heater
as is possible to obtain.

Diagram of Circuits

for

Adiabatic

Calorimeter

Temp. Measurement.

outer Heater Circuit.

Potentiometer

Temp. Diff. Measure.

Storage Cells

Depolariser

R_1

R_2

.1325 ohms

100

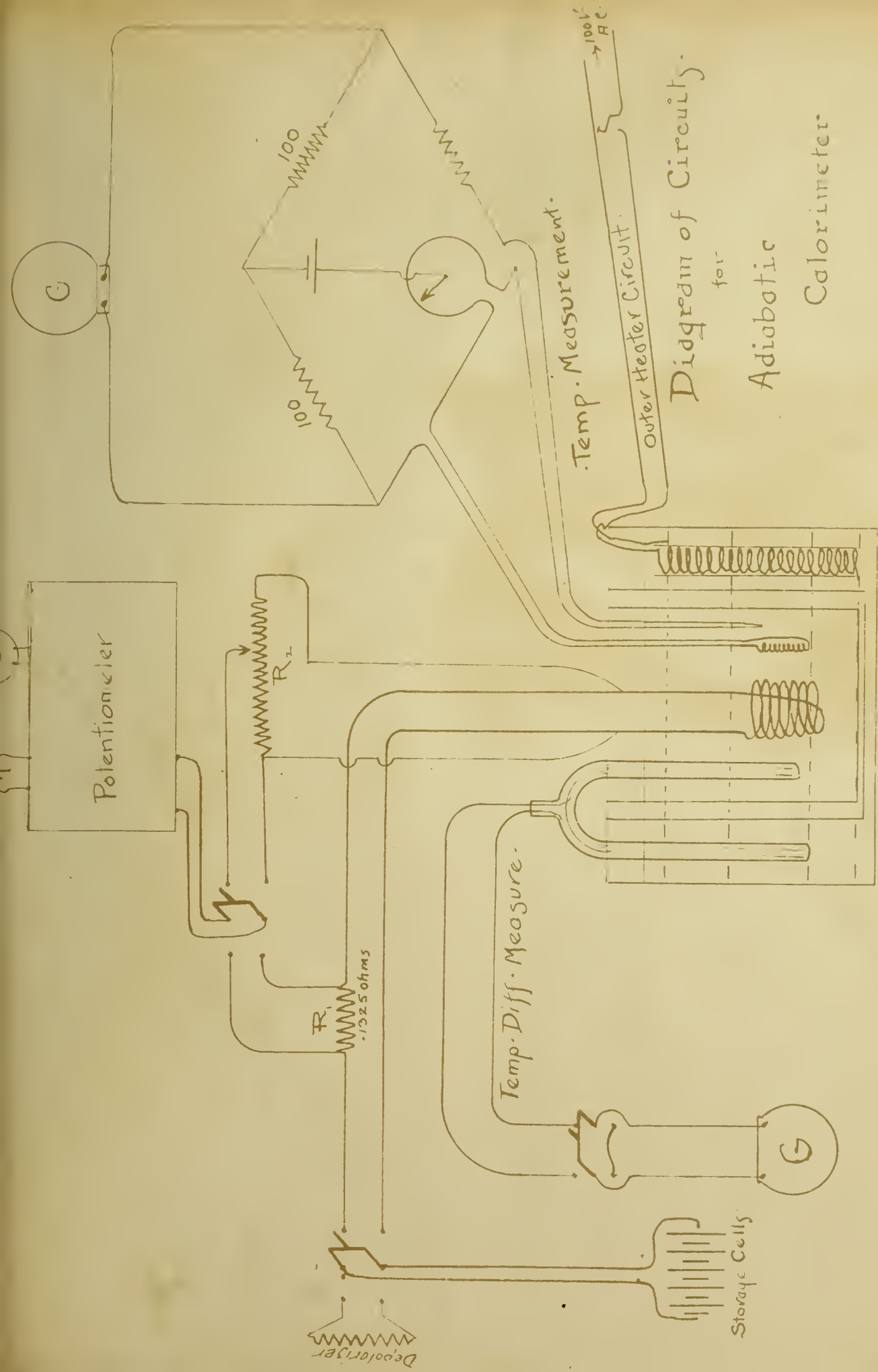100

100

→ 100 ⊢
A C

G

G

Fig. III.

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VI.- Measurement of the energy of dilution.

The addition of energy by means of an electrical cur-
rent embodies the following ideas: First of all, the whole
method employed is a relative one and the only absolute val-
ues needed are for the amounts of the liquids used in the
dilution, their strength, and the values of time, current,
and potential, used when the energy is applied by the current
from storage cells. When a given amount of water is diluted
in a given amount of a known solution, a relative temperature
rise is observed which is proportional to the total heat cap-
acity of the entire system. If this temperature rise were
figured out by calibrating the thermometer more accurately
to degrees centigrade, and this rise multiplied by the heat
capacity of the system, the energy could be determined by this
manner. This is unnecessary, however, as the total heat cap-
acity is a constant throughout the entire run. A second rel-
ative rise is taken by passing in current from storage cells,
this rise being considerably larger than that due to the
dilution, so that very accurate measurements of the energy
can be obtained. Time is taken to fifths of a second by a
stop watch and current and e.m.f. readings are taken as often
as is necessary, (i.e. readings must of course be taken more
frequently if the values are changing slightly). The e.m.f.
values are taken by merely running a parallel circuit through
a high resistance. The value of current is obtained by measur-
ing the drop across a known resistance (a resistance of .1325
ohms was used in this work). Both of these potential values
are compared on a Leeds and Northrup potentiometer against a

constant cell, which cell has been compared with a standard
cell (Weston cell No. 2328). This last comparison can be
made at any time during the run by simply throwing a switch
and this is done from time to time to be sure of correct
values. The potentiometer has been calibrated by the Bureau
of Standards and the standard cell is one giving a constant
voltage of 1.0187_7 volts. All precautions have been taken
to obtain the most accurate measure of energy possible.
Using the data just obtained for the energy required for the
large relative rise, the energy for the heat of the dilution
can be obtained by a simple proportion. The assumption is
made that specific heats do not vary enough in the range
of temperature used to affect the results. (The maximum
rise is less than 1 degree C.)

It is necessary that the current from the cells be
polarized before a run is made; otherwise the fluctuations
in current are so great that no accuracy can be obtained
in the measurement of energy.

Description of a run

In the trial run it will be assumed that the data on
the heat of dilution is desired at 20° C. and that the room
temperature is about 18.5° C. Various alterations of the
method must be made where these factors are different, but
these will be mentioned each in the proper place. The calor-
imeter is first set up with great care that no moisture is
in the space J, and that the interior of the vessel V_1 is
entirely dry. The water for the bath Y is poured into the
space surrounding the vessel V_2 and allowed to cover the
calorimeter to a depth of about an inch. The bath Y should

be at about 19.5° C. The solution to be diluted (4 normal
methyl alcohol was used, for example) which has been weighed
to the nearest $\frac{1}{2}$ gram and brought to about 19.8°C. is allowed
to run into the vessel V_2 through the opening for that pur-
pose. If necessary the inner heater may be used to bring the
temperature up to exactly 20° C. as can be observed by in_
serting a thermometer into the liquid X. The water for dilut-
ing the solution is also weighed to the nearest .1 gram and
is allowed to run into the innermost vessel, V_1. The platinum
resistance thermometer and the thermo-couple for recording
the temperature difference between the baths are next insert-
ed and the stirring mechanism started and adjusted so as to
give 60 strokes per minute. Starting with about .2° C. diff-
erence between the baths X and Y, the outer one being the
cooler, temperture readings with the resistance ther mometer
are taken simultaneously with temperature difference readings.
By heating slowly with the outer heater the corressponding
bath Y, a temperature difference will be reached at which
the temperature of X does not change 1/10,000 of a degree
even over a long period of time. This difference, then, is
the one which under the given conditions exactly counter-
balances the tendency to heat up the inner solution by stir-
ring, and also compensates for any evaporation effects from
the solution X. If the room temperature is much warmer than
that at which a determination is desired, ice or cold water
in the space Z will keep the bath Y at its proper temperature
or near enough so that the heater can by frequent application
establish the difference. The temperature difference observed
for any conditions may be deviated from to a small extent

without any effect on the temperature of the bath X which
is being read to 1/10,000 of a degree.

When a series of constant temperature readings show
that an equilibrium has been reached between the heat given
off by the stirring of the liquid X and the heat given off
by the inner vessel to the bath Y, then the cork M is pushed
out by means of the brass rod centered on it. Immediately
the two solutions begin to mix and heat is evolved as is
shown by the readings of the platinum resistance thermometer.
During the temperature rise, heat must be added to the bath
Y so that the temperature difference is kept at the amount
determined upon, as was described.above. Finally when mix-
ing is complete, (this can be assured by lowering the vessel
V_1 until the liquid covers it and allowing time for thorough
mixing) a new temperature is reached and remains constant as
beforeas long as the temperature difference between X and Y
is maintained. The relative value of the rise which is to be
compared to the rise due to the passing of a known amount
of current, is the difference between the first and the
second constant readings.

Where the temperature is to be measured to such an
accuracy there might be some little doubt as to whether
the liquids Q and X were really at the same temperature
before dilution or whether they might be at so small a
difference as to fail to equalize. An experiment showed
that they were at the same temperature when constant readings
of the temperature of X were obtained before dilution or
at least that if any temperature difference existed, that
its effect on so large a mass of liquid as X could not be

detected. Data for the experiment: Pure water in X and Q.

Time (minutes)		Temperature (bridge units)
0.0		.2157
1.0		.2157
4.5		.2157
5.0	Mixing took place	.2157
6.0		.2157
8.5		.2157
10.0		.2157

A change of .0001 in the above table represents 1/100,000
of an ohm or 1/10,000 of a degree C.(approximately) with
the thermometer used.

The table on the next page gives a trial run showing
typical results such as were obtained in a large number of
runs. The first column simply gives the time as recorded by
an ordinary watch. The figures in the second column refer
to the units on the bridge and represent approximately 1/10,000
of a degree C. for each .00001 though the bridge was not cali-
brated for temperature accurately for reasons which have been
given. The third column gives the "constant difference"readings,
and the first few readings show how these were taken until
the proper difference showed up (when the temperature readings
in column Two became constant). The fourth and fifth columns
give the potential and current values in arbitrary units on
the potentiometer, showing the data for calculating the heat
capacity when the current was passed into the calorimeter .
The accurate measurement of time during which the current
passed was obtained by stop watch, the readings of which appear
in the last column. In this run the current was passed into
the calorimeter twice and two temperature rises were taken.
This was not necessary and was not followed out in all the
runs.

A trial run with the calorimeter, using 4 normal methyl alcohol solution.

Actual Time	Temp. in Resist. units	Diff. in Galv. scale units	E.M.F.	-I-	Time, stop-watch
10:00:00 pm.	R+.01887	1.60			
1:30	.01885	1.60			
3:00	.01883	1.60			
5:10	.01880	1.20			
7:00	.01875	1.17			
8:50	.01874	1.15			
11:00	.01867	1.10			
12:30	.01865	1.10			
13:45	.01865	1.00			
15:30	.01865	1.00			
18:30	.01865	.97			
19:40	.01863	.90			
20:20	.01864	.90			
23:40	.01864	.90 ← Dilution took place.			
27:50	.02297	.90			
29:45	.02296	.85			
31:20	.02296	.78			
33:10	.02296	.75			
35:00	.02296	.75	34305	34225	00:00
37:00	Heating begins		306	225	20:00
38:30			306	226	3:30
40:00			307	226	5:00
42:00			307	226	7:00
43:30			308	226	8:30
44:10			308	226	9:10
45:00			309	227	10:00
46:00			309	226	11:00
47:30			309	227	12:30
48:00	Heating stops.		310	227	13:30
50:36.8	.05737	.80			15:36.8
52:30	.05738	.75			
53:00	.05738	.75			
53:30	.05738	.75			
55:00	Heating begins again		34315	233	00:00
56:30			314	233	1:30
57:30			312	233	2:30
58:15			314	232	3:15
11:00:00			315	232.5	5:00
2:50			315	232	7:50
6:50			315	232	11:50
10:00			316	232	15:00
13:00.2	Heating stopd		315	232	18:00.2
14:00	.09994	.75			
15:30	.09996	.75			
16:15	.09996	.75			
17:30	.09996	.75			

Conclusions of the Thesis.

The foregoing experiments and work show that a combin-
ation of the adiabatic principle with the platinum resistance
thermometer, and the electrical determination of the heat
capacity of the calorimeter is suitable for the determination
of the small energy changes resulting, for instance, from
the dilution of moderately concentrated alcohol solutions.

In the work on the calorimeter several advantageous
changes might be made and in the work which will be continued
many of these will be worked out. We regret that the time
was not sufficient to obtain some actual results and data
on dilutions but these will be obtained with the calorimeter
later. The calorimeter itself has, we believe, been worked
out on a practical basis and has shown itself to be capable
of accomplishing the results desired.